

CLAIMS:

What is claimed is:

1. A method, comprising:

electrocodepositing particles of at least one quasicrystalline metal alloy and at least one elemental metal onto a working electrode disposed in an electroplating bath, wherein the electroplating bath comprises a solvent, ions of the at least one elemental metal dissolved in the solvent, and the particles of at least one quasicrystalline metal alloy suspended in the solvent.

2. The method of claim 1, wherein the working electrode has an electronically conducting surface.

3. The method of claim 2, wherein the electronically conducting surface comprises a material selected from metals, alloys, graphite, carbon-carbon composites, and combinations thereof.

4. The method of claim 1, wherein the at least one elemental metal is selected from manganese, iron, cobalt, chromium, nickel, copper, zinc, and combinations thereof.

5. The method of claim 1, wherein the electroplating bath is selected from an electrolytic deposition bath, an electroless deposition bath, and mixtures thereof.

6. The method of claim 1, wherein the electroplating bath is suitable for plating the at least one elemental metal, wherein the at least one elemental metal is selected from nickel, copper, and combinations thereof.

7. The method of claim 1, wherein the temperature of the electroplating bath during the electrocodeposition does not exceed the melting point of the particles of the at least one quasicrystalline metal alloy or the melting point of the working electrode.

8. The method of claim 1, wherein the temperature of the electrocodeposition bath during the electrocodeposition does not exceed 100 °C.
9. The method of claim 1, wherein the at least one quasicrystalline metal alloys include aluminum-transition metal alloys.
10. The method of claim 9, wherein the aluminum-transition metal alloys are selected from Al-Cu-M, Al-Pd-M and combinations thereof, where M is a transition metal selected from Fe, Ru, Ni, Mn, Cr, Co and combinations thereof.
11. The method of claim 9, wherein the quasicrystals are ternary, quaternary and higher alloys.
12. The method of claim 9, wherein the quasicrystals include up to about 10 atomic percent of a transition metal selected from Ti, V, Cr, Mn, Co, Ni, Ta, W, Nb, Mo, Zr and combinations thereof.
13. The method of claim 9, wherein the quasicrystals include B, Si or combinations thereof.
14. The method of claim 1, wherein the electroplating bath comprises between 25 and 150 grams of quasicrystalline metal alloy particles per liter of the electroplating bath.
15. The method of claim 1, wherein the working electrode is a substrate selected from copper, aluminum, an alloy of aluminum, carbon or graphite, cast iron, wrought iron, carbon steels, stainless steels, copper/tin alloys, copper/zinc alloys, copper/nickel alloys, doped or undoped semiconductors, polymer/carbon composites, polymer/graphite composites, polymer/metal composites, and metal/metal composites.
16. The method of claim 1, wherein the working electrode is selected from polymers and polymer composites.

17. The method of claim 16, wherein the working electrode is a polymer composite comprising carbon or metal.
18. The method of any one of the preceding claims, further comprising:  
applying an electroless or electrolytic strike on the working electrode prior to the electrocodepositing step, wherein the strike comprises a metal selected from zinc, nickel, copper, platinum, cobalt, gold and combinations thereof.
19. The method of claim 18, wherein the working electrode is an aluminum alloy 3004 substrate, and the strike includes electroless zincate followed by electroless copper.
20. The method of claim 1, wherein the electroplating bath is aqueous.
21. The method of claim 20, wherein the at least one elemental metal is selected from chromium, manganese, iron, cobalt, nickel, copper, zinc, and combinations thereof.
22. The method of claim 21, wherein the concentration of the metal ions in the electroplating bath is between 500 and 20,000 ppm.
23. The method of claim 1, wherein the dissolved metal ions are in the form of a metal sulfate, metal sulfamate, metal citrate, metal chloride, metal bromide, metal nitrate, or combinations thereof.
24. The method of claim 1, wherein the electroplating bath comprises aqueous nickel sulfate.

25. The method of claim 24, wherein the electroplating bath comprises between 2 and 12 grams of nickel sulfate per liter of the electroplating bath.
26. The method of claim 1, wherein the electroplating bath further comprises a reducing agent, a buffering agent, or a combination thereof.
27. The method of claim 1, wherein the electroplating bath further comprises a buffering agent selected from hypophosphite, formaldehyde, acetate, citrate, boric acid, and combinations thereof.
28. The method of claim 1, further comprising:  
agitating the electroplating bath to suspend the quasicrystalline metal alloy particles.
29. The method of claim 1, wherein the quasicrystalline metal alloy particles have an average particle size less than 50 microns.
30. The method of claim 1, wherein the quasicrystalline metal alloy particles have an average particle size less than 20 microns.
31. The method of claim 28, wherein the electroplating bath comprises between 25 and 150 grams of suspended quasicrystalline metal alloy particles per liter of electroplating bath.
32. The method of claim 1, wherein the at least one quasicrystalline metal alloy is selected from  $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_{12}$ ,  $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ ,  $\text{Al}_{59}\text{Cu}_{25.5}\text{Fe}_{12.5}\text{B}_3$ ,  $\text{Al}_{64}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ , and combinations thereof.

33. The method of claim 2 or any claim dependent thereon, further comprising:  
maintaining the electroplating bath at a pH between 2 and 7.
34. The method of claim 33, further comprising:  
adding aqueous  $K_2CO_3$  or  $H_2SO_4$  to the bath to maintain the pH.
35. The method of claim 2, further comprising:  
maintaining the temperature of the electroplating bath during electrocodeposition between 10 and 70 °C.
36. The method of claim 11, further comprising:  
providing a counter electrode comprising iron, cobalt, nickel, copper, zinc, platinized titanium, or ruthenium/iridium oxide-coated titanium metal, or a combination thereof.
37. The method of claim 1, wherein the working electrode is electronically conductive.
38. The method of claim 1, further comprising:  
applying a direct current between the working electrode and the counter electrode at a potential of between 1.5 and 7 volts.
39. The method of claim 1, further comprising:  
applying a current density to the working electrode between 2 and 100 mA/cm<sup>2</sup> for a period of 5 to 90 minutes.

40. The method of claim 1, further comprising:  
applying a current density to the working electrode between 2 and 100 mA/cm<sup>2</sup>.
41. The method of claim 1, further comprising:  
moving at least one electrode during the electrocodeposition.
42. The method of claim 1, further comprising:  
electroplating a metal seal layer over a layer comprising the electrocodeposited quasicrystalline metal alloy particles.
43. The method of claim 42, wherein the metal seal layer is electroplated in a separate seal bath.
44. The method of claim 43, further comprising:  
alternating the use of the seal bath and the electroplating bath containing the suspended particles of a quasicrystalline metal alloy.
45. The method of claim 44, further comprising:  
repeating the alternating use of the baths until a desired coating thickness is obtained.
46. The method of claim 1, further comprising:  
short-cycle ramping of a DC current used for the electrocodeposition.
47. The method of claim 46, further comprising:  
repeatedly ramping the DC current between essentially zero current and a target current density.

48. The method of claim 47, wherein the target current density is about 40 mA/cm<sup>2</sup>.
49. The method of claim 47, wherein the ramping occurs in cycles between 10<sup>-2</sup> and 10<sup>5</sup> Hertz.
50. The method of claim 1, wherein the electrocodeposition occurs under constant current conditions.
51. The method of claim 50, wherein the constant current is between 2 and 100 mA/cm<sup>2</sup>.
52. The method of claim 2, further comprising:  
agitating the electrolyte solution.
53. The method of claim 1, wherein the at least one quasicrystalline metal alloy is Al<sub>65</sub>Cu<sub>23</sub>Fe<sub>12</sub>.
54. The method of 1, wherein the at least one quasicrystalline metal alloy is Al<sub>70</sub>Cu<sub>10</sub>Fe<sub>10</sub>Cr<sub>10</sub>.
55. The method of claim 1, wherein the ions of the at least one elemental metal include nickel ions.
56. The method of claim 55, wherein the nickel ion concentration is between 2 and 10 grams per liter of electroplating bath.
57. The method of claim 1, wherein the at least one elemental metal includes copper.
58. The method of claim 1, further comprising:  
simultaneously performing the electrocodepositing step on multiple working electrodes in the same electroplating bath.

59. The method of claim 1, further comprising:  
annealing the particles of the at least one quasicrystalline metal alloy.
60. The method of claim 59, wherein the at least one quasicrystalline metal alloy is converted from the beta-phase to the quasicrystalline phase.
61. The method of claim 59, wherein the annealing is performed prior to electrocodepositing the particles.
62. The method of claim 59, wherein the annealing is performed after electrocodepositing the particles.
63. The method of claim 59, wherein the annealing is performed before and after electrocodepositing the particles.
64. The method of claim 59, wherein the at least one quasicrystalline metal alloy is annealed at a temperature between 500 and 700°C.
65. The method of claim 59, characterized in that the annealing increases the ratio of quasicrystalline phase in the particles.
66. The method of claim 59, wherein the annealing is performed under an inert gas atmosphere.
67. The method of claim 1, further comprising:  
masking a portion of the working electrode to prevent electrocodeposition.
68. The method of claim 1, wherein the electroplating bath contains copper sulfate.
69. The method of claim 68, wherein the copper sulfate has a concentration between 0.1 and 0.6 grams of copper per liter of the bath.



70. The method of claim 1, further comprising a preliminary step selected from bead blasting the surface of the substrate, degreasing the substrate prior to electrocodepositing, and combinations thereof.
71. The coated working electrode prepared by the method of claim 1.
72. The coated working electrode prepared by the method of claim 4.
73. The coated working electrode prepared by the method of claim 29.
74. The coated working electrode prepared by the method of claim 32.
75. The coated working electrode prepared by the method of claim 59.
76. A coating composition, comprising:  
between 25 and 90 percent by mass of particles of at least one quasicrystalline metal alloy within a metal matrix including at least one elemental metal.
77. The composition of claim 76, wherein the particles have an average size less than 20 microns.
78. The composition of claim 76, wherein the particles comprise between 40 and 60 percent by mass of the quasicrystals.
79. The composition of claim 76, wherein the at least one elemental metal is selected from nickel, copper, and combinations thereof.
80. The composition of claim 76, wherein the at least one quasicrystalline metal alloy is selected from  $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_{12}$ ,  $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ ,  $\text{Al}_{59}\text{Cu}_{25.5}\text{Fe}_{12.5}\text{B}_3$ ,  $\text{Al}_{64}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ ,  $\text{Al}_{70}\text{Cu}_{10}\text{Fe}_{10}\text{Cr}_{10}$ , and combinations thereof.

81. The composition of claim 76, wherein the at least one quasicrystalline metal alloy includes an aluminum-transition metal alloy.
82. The composition of claim 81, wherein the aluminum-transition metal alloy is selected from Al-Cu-M, Al-Pd-M and combinations thereof, where M is a transition metal selected from Fe, Ru, Ni, Mn, Cr, Co and combinations thereof.
83. The composition of claim 76, further comprising:  
a metal seal layer deposited over the metal matrix.
84. The composition of claim 76, wherein the quasicrystal particles are tiled.
85. The composition of claim 76, wherein the metal matrix has a thickness less than 40  $\mu\text{m}$ .
86. A composition, comprising:  
particles of at least one quasicrystalline metal alloy within a metal matrix including at least one elemental metal, wherein the composition is characterized by a hardness greater than 6 GPa, a coefficient of friction less than 0.2, and a contact angle greater than 100 degrees.
87. The composition of claim 86, characterized in that the particles of quasicrystalline metal alloys are tiled.
88. The composition of claim 86, characterized in that the composition has a hardness between 6 and 10 GPa.
89. The composition of claims 86, characterized in that the composition produces an XRD spectra substantially the same as the XRD spectra produced by the bulk quasicrystalline material.
90. The composition of claim 86, wherein the coefficient of friction is less than 0.1.

91. The composition of claim 86, wherein the coefficient of friction is less than 0.05.
92. The composition of claim 86, wherein the at least one elemental metal is selected from nickel, copper, and combinations thereof.
93. The composition of claim 86, characterized by a contact angle greater than 110 degrees.